



# DECLARATION

I, Youngsun JUNG, of SHIGA INTERNATIONAL PATENT OFFICE, 1-9-2, Marunouchi, Chiyoda-ku, Tokyo 100-6620, Japan, understand both English and Japanese, am the translator of the English document attached, and to hereby declare and state that the attached English document contains an accurate translation of the official certified copy of Japanese Patent Application No. 2003-204620 and that all statements made herein are true to the best of my knowledge.

Declared in Tokyo, Japan

This 27th day of January, 2009

A handwritten signature in black ink, appearing to be "Youngsun JUNG", written over a horizontal dotted line.

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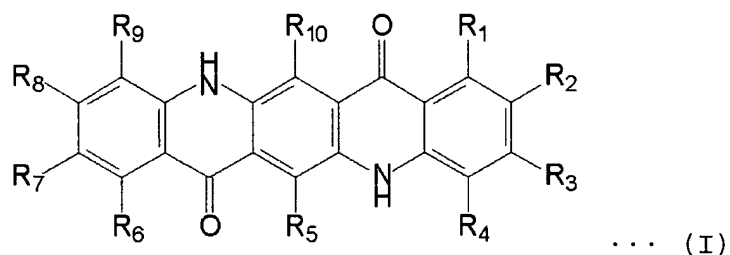
[Title of the Invention] WATER-BASED INK COMPOSITION FOR INK-JET RECORDING, WATER-BASED PIGMENT DISPERSION FOR INK-JET INK TO PRODUCE INK COMPOSITION AND COLORED KNEADED MIXTURE FOR INK-JET INK AND METHOD OF PRODUCING THE SAME

[Claims]

[Claim 1]

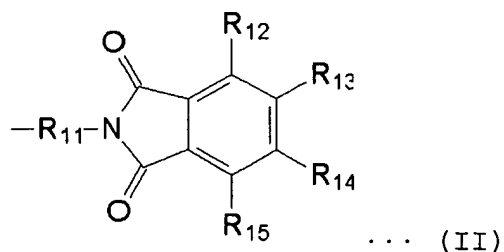
A colored kneaded mixture for ink-jet ink, comprising:  
 a quinacridone-based pigment (a),  
 a compound (b) represented by the formula (I):

[Chemical 1]



wherein  $R_1$  to  $R_{10}$  each independently represents hydrogen, fluorine, chlorine, bromine, iodine, a methyl group or an alkyl group having 2 to 8 carbon atoms, or a group represented by the formula (II):

[Chemical 2]



wherein  $R_{11}$  represents a methylene group or an alkylene group or alkenyl group having 2 to 8 carbon atoms, and  $R_{12}$  to  $R_{15}$  each independently represents hydrogen, fluorine, chlorine, bromine, iodine, a methyl group or an alkyl group having 2 to 8 carbon atoms, or phenyl group;

and at least one of  $R_1$  to  $R_{10}$  is the group represented by the formula (II),

a styrene-based resin (c), and

an alkali metal hydroxide (d), wherein

the styrene-based resin (c) is a copolymerized resin of (i) 60% by mass or more of a styrene-based monomer unit based on all monomer components and (ii) a monomer unit containing an unsaturated aliphatic carboxylic acid having a radical polymerizable double bond, and has an acid value of 50 to 300 and a weight-average molecular weight of 7,500 to 40,000.

[Claim 2]

The colored kneaded mixture for ink-jet ink according to claim 1, wherein the styrene-based resin (c) is a copolymerized resin of 60% by mass or more of a styrene-based monomer based on all monomer components, and a monomer containing an acrylic acid and a methacrylic acid.

[Claim 3]

The colored kneaded mixture for ink-jet ink according

to claim 2, wherein the total content of the styrene-based monomer, the acrylic acid and the methacrylic acid in the styrene-based resin (c) is 95% by mass or more based on all monomer components.

[Claim 4]

The colored kneaded mixture for ink-jet ink according to claim 1, wherein the quinacridone-based pigment (a) is C.I. Pigment Red 122.

[Claim 5]

The colored kneaded mixture for ink-jet ink according to claim 1 or 2, wherein the quinacridone-based compound having a substituent group comprising a phthalimido skeleton is phthalimidomethylated 3,10-dichloroquinacridone.

[Claim 6]

The colored kneaded mixture for ink-jet ink according to claim 1, wherein the amount of the alkali metal hydroxide is 0.8 to 1.2 times the amount required to neutralize all carboxyl groups of the styrene-based resin (c).

[Claim 7]

The colored kneaded mixture for ink-jet ink according to claim 1, wherein it further comprises a humectant.

[Claim 8]

A water-based pigment dispersion for ink-jet ink, which is produced by using the colored kneaded mixture for ink-jet ink according to any one of claims 1 to 7.

[Claim 9]

An ink composition for ink-jet recording, which is produced by using the water-based pigment dispersion for ink-jet ink according to claim 8.

[Claim 10]

The ink composition for ink-jet recording according to claim 9, which is used for a thermal jet type printer.

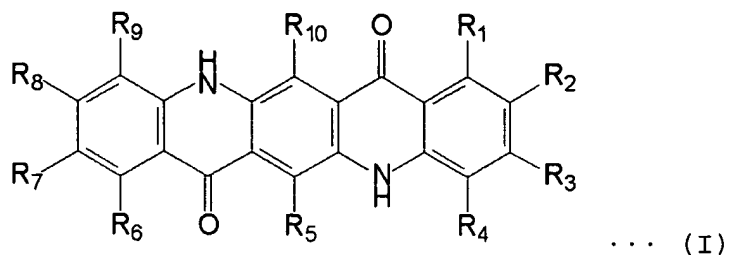
[Claim 11]

A method of producing a colored kneaded mixture for ink-jet ink, comprising a kneading step for kneading an aqueous solution or an organic solvent solution comprising:

a quinacridone-based pigment (a),

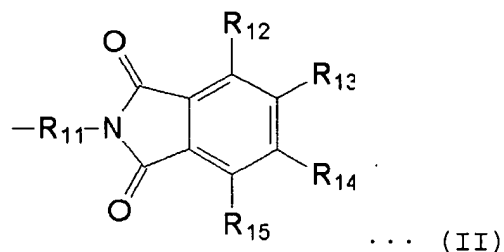
a compound (b) represented by the formula (I):

[Chemical 3]



wherein  $R_1$  to  $R_{10}$  each independently represents hydrogen, fluorine, chlorine, bromine, iodine, a methyl group or an alkyl group having 2 to 8 carbon atoms, or a group represented by the formula (II):

[Chemical 4]



wherein  $R_{11}$  represents a methylene group or an alkylene group or alkenyl group having 2 to 8 carbon atoms, and  $R_{12}$  to  $R_{15}$  each independently represents hydrogen, fluorine, chlorine, bromine, iodine, a methyl group or an alkyl group having 2 to 8 carbon atoms, or phenyl group;

and at least one of  $R_1$  to  $R_{10}$  is the group represented by the formula (II),

a styrene-based resin (c), and

an alkali metal hydroxide (d),

to obtain a colored kneaded mixture, wherein

the styrene-based resin (c) is a copolymerized resin of



(i) 60% by mass or more of a styrene-based monomer unit based on all monomer components and (ii) a monomer unit containing an unsaturated aliphatic carboxylic acid having a radical polymerizable double bond, and has an acid value of 50 to 300 and a weight-average molecular weight of 7,500 to 40,000.

[Claim 12]

A method of producing a water-based pigment dispersion for ink-jet ink, comprising a dispersing process for dispersing the colored kneaded mixture for ink-jet ink produced by the method of producing a colored kneaded mixture for ink-jet ink according to claim 11 in an aqueous medium.

[Detailed Description]

[0001]

[Technical Field]

The present invention relates to a water-based pigment dispersion for red or magenta ink-jet ink, a colored kneaded mixture to produce a water-based ink composition for ink-jet recording, and a method of producing the colored kneaded mixture, and in particular, relates to a ink composition suitable for a thermal jet recording type printer.

[0002]

[Background Art]

A water-based ink, in which water is used as a main solvent, has been mainly used for ink-jet recording as a non-industrial ink for ink-jet recording, since the water-based ink has no or more reduced risk of fire or toxic properties such as mutagenicity shown in an oil-based ink, causing the water-based ink preferable.

In the past, dye was used as a coloring agent for the water-based ink for ink-jet recording, since the dissolution stability is high and clogging of nozzle is almost not occurred and therefore good coloring property is obtained and high-quality of print becomes possible. However, in using dye, there was a problem that water resistance and light fastness were not enough, and therefore dye could not be used for an industrial purpose. Further, in recent years, the

demand for good water resistance, light fastness and long-term stability of image quality has been also requested for home use. The conversion of coloring agent from dye to pigment has been actively challenged. The pigmented ink is expected to have excellent water resistance and light fastness, but problems such as aggregation or sedimentation of the pigment and clogging of a nozzle is easily occurred. To solve these problems, various methods of dispersing a pigment in an aqueous medium using a polymer dispersant as a dispersant have been studied. However, even if dispersion is conducted by using only the polymeric dispersant through disperser, it was hard to disperse the pigment stably over a long time.

[0003]

For example, as this method wherein a pigment is dispersed in an aqueous medium by using a polymer dispersant, there has been proposed a method of dissolving an aqueous polymer dispersant in water by using a basic component to obtain an aqueous solution, adding a pigment, sufficiently stirring the mixture, and further using a high-speed sand mill and the likes which enable the dispersion efficiency high. However, since the dispersion does not necessarily proceed with high shearing force, crushing strength in this dispersion method by sand mill, long dispersing process time is required, causing a problem such as low production

efficiency. In addition, it happens that crude particles remains even in the water-based pigment dispersion obtained by above, both the initial dispersibility and the dispersion stability were not sufficient.

[0004]

Trials using various pigment derivatives as the dispersant, were made so as to stably maintain a dispersion state of the pigment for a long period. For example, there is proposed a method of utilizing electrostatic repulsion of a sulfonic acid group-containing pigment derivative adsorbed onto the surface of a pigment using a pigment and a sulfonic acid group-containing pigment derivative (see Patent Document 1). According to this method, although dispersion stability of a colorant is improved, printed matter obtained has high affinity with water because of the presence of a polar functional group on the surface of the colorant. Furthermore, comparing with an ink using a pigment itself as a coloring material, there may arise a problem of poor water resistance.

To attain excellent dispersibility and dispersion stability of a water-based pigment dispersion or recording ink, which contains a quinacridone-based pigment as the colorant, there are proposed an encapsulated pigment dispersion wherein a quinacridone-based pigment and a dimethylaminomethylated quinacridone compound are used in combination (see Patent Document 2), and a water-based

pigment dispersion containing a quinacridone-based pigment, a phthalimidomethylated quinacridone-based compound, a quinacridonesulfonic acid-based compound, and an anionic group-containing organic polymeric compound having a glass transition point of -20 to 60°C (see Patent Document 3). However, the magenta water-based pigment dispersion described in these publications was not sufficient in dispersion level and dispersion stability. In particular, when the dispersion was used for the thermal jet type ink-jet recording, thermal stability was not sufficient.

[0005]

Meanwhile, it has been known that a water-based pigment dispersion for ink-jet ink using styrene-acrylic resin (styrene/acrylic acid/methacrylic acid = 77/10/30, molecular weight 50,000) as resin to disperse the quinacridone-based pigment (see Patent Document 4). However, the magenta water-based pigment dispersion described in the publication was not sufficient in dispersion level and dispersion stability. In particular, when the dispersion was used for the thermal jet type ink-jet recording, discharge stability was not sufficient.

In addition, it has been known that a water-based pigment dispersion for ink-jet ink using styrene-acrylic resin (styrene/acrylic acid/methacrylic acid = 77/10/30, molecular weight 7,200 and 8,300) as resin to disperse the

quinacridone-based pigment (see Patent Documents 5 and 6). However, any specific method for improvement of the dispersion stability of the magenta water-based pigment dispersion described in the publications was not proposed.

As above, the publications do not disclose or suggest any meaningful clues to obtain an improvement of the dispersion stability of the water-based ink composition for ink-jet ink recording, in particular, a good thermal jet type ink-jet recording.

[0006]

[Patent Document 1]

Japanese Patent Application, First Publication No. 2002-241638

[Patent Document 2]

Japanese Patent Application, First Publication No. Hei 9-151342

[Patent Document 3]

Japanese Patent Application, First Publication No. 2000-191974

[Patent Document 4]

Japanese Patent Application, First Publication No. 2000-186244 (Example 5)

[Patent Document 5]

Japanese Patent Application, First Publication No. 2001-164165 (Examples)

[Patent Document 6]

Japanese Patent Application, First Publication No. 2003-41178

(Examples)

[0007]

[Problems to be solved by the Invention]

Accordingly, an object of the present invention is to provide a red or magenta coloring pigment dispersion for ink-jet ink, which is excellent in dispersibility and dispersion stability and is less likely to cause an increase in particle size even when allowed to stand at high temperature for a long period, and also which is less likely to cause an increase in viscosity and is excellent in storage stability, and a color kneaded mixture for ink-jet ink used to produce a water-based ink composition for ink-jet recording using the same.

In particular, an object of the present invention is to provide a colored kneaded mixture for ink-jet in order to obtain a pigment dispersion for ink-jet and a water-based ink composition for ink-jet recording suitable for thermal jet.

[0008]

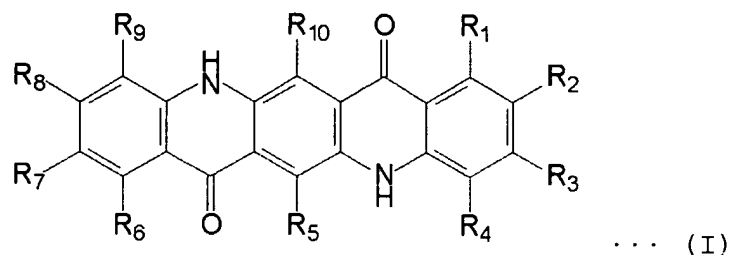
[Means for Solving the Problems]

The present inventors have intensively researched about the above problems and found that these problems can be solved by using the following means.

Thus, the present invention provides a colored kneaded

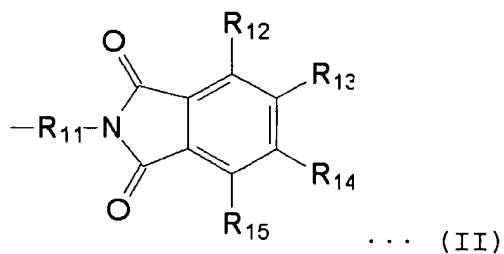
mixture for ink-jet ink, comprising a quinacridone-based pigment (a), a compound (b) represented by the formula (I):

[Chemical 5]



wherein R<sub>1</sub> to R<sub>10</sub> each independently represents hydrogen, fluorine, chlorine, bromine, iodine, a methyl group or an alkyl group having 2 to 8 carbon atoms, or a group represented by the formula (II):

[Chemical 6]



wherein R<sub>11</sub> represents a methylene group or an alkylene group or alkenyl group having 2 to 8 carbon atoms, and R<sub>12</sub> to R<sub>15</sub> each independently represents hydrogen, fluorine, chlorine, bromine, iodine, a methyl group or an alkyl group having 2 to 8 carbon atoms, or phenyl group;

and at least one of R<sub>1</sub> to R<sub>10</sub> is the group represented by the formula (II),

a styrene-based resin (c), and an alkali metal



hydroxide (d), wherein the styrene-based resin (c) is a copolymerized resin of (i) 60% by mass or more of a styrene-based monomer unit based on all monomer components and (ii) a monomer unit containing an unsaturated aliphatic carboxylic acid having a radical polymerizable double bond, and has an acid value of 50 to 300 and a weight-average molecular weight of 7,500 to 40,000.

[0009]

The compound (b) represented by the formula (I) is compatible with the styrene-based resin (c) constituting of 60% by mass or more of a styrene-based monomer unit, an acrylic acid monomer unit and a methacrylic acid monomer unit used in the present invention, and supplements the function of dispersion stability of the resin, causing an improvement in dispersion stability of the water-based ink composition containing the quinacridone-based pigment. In addition, when the resin has a high glass transition temperature ( $T_g$ ), the water-based ink composition becomes to have further high heat stability, and it can be preferably used in the thermal jet type ink-jet recording.

[0010]

The present invention also provides a method of producing the colored kneaded mixture for ink-jet ink, comprising a kneading step for kneading an aqueous solution or an organic solvent solution comprising the quinacridone-

based pigment (a), the compound (b) represented by the formula (I), the styrene-based resin (c), and the alkali metal hydroxide (d), to obtain the colored kneaded mixture, wherein the styrene-based resin (c) is a copolymerized resin of (i) 60% by mass or more of a styrene-based monomer unit based on all monomer components and (ii) a monomer unit containing an unsaturated aliphatic carboxylic acid having a radical polymerizable double bond, and has an acid value of 50 to 300 and a weight-average molecular weight of 7,500 to 40,000.

[0011]

[Best Mode for Carrying out the Invention]

The water-based pigment dispersion for ink-jet ink in the present invention will be described in more detail. An "water-based pigment dispersion for ink-jet ink" is abbreviated to an "ink composition", and a "colored kneaded mixture for ink-jet ink" in order to produce the water-based pigment dispersion for ink-jet ink is abbreviated to a "colored kneaded mixture".

[0012]

As the quinacridone-based pigment (a) in the present invention, any conventionally known one can be used. Specific examples thereof include dimethylquinacridone-based pigments such as C.I. Pigment Red 122; dichloroquinacridone-based pigments such as C.I. Pigment Red 202 and C.I. Pigment

Red 209; non-substituted quinacridones such as C.I. Pigment Violet 19; and mixtures or solid solutions of at least two kinds of pigments selected from among these pigments. The pigment may be a dry pigment in the form of powder, granule or bulk, or may be in the form of a wet cake or slurry.

Among the quinacridone-based pigments, C.I. Pigment Red 122 is preferably used.

[0013]

The styrene-based resin (c) used in the present invention is a copolymerized resin of (i) 60% by mass or more of a styrene-based monomer based on all monomer components, (ii) a monomer containing an unsaturated aliphatic carboxylic acid having a radical polymerizable double bond, and has an acid value of 50 to 300 and a weight-average molecular weight of 7,500 to 40,000.

[0014]

As the styrene-based monomer, known compounds can be used. For example, there can be used alkylstyrenes such as styrene,  $\alpha$ -methylstyrene,  $\beta$ -methylstyrene, 2,4-dimethylstyrene,  $\alpha$ -ethylstyrene,  $\alpha$ -butylstyrene and  $\alpha$ -hexylstyrene; halogenated styrenes such as 4-chlorostyrene, 3-chlorostyrene and 3-bromostyrene; and 3-nitrostyrene, 4-methoxystyrene and vinyltoluene.

[0015]

The content of the styrene-based monomer as a material

of the styrene-based resin (c) is preferably from 60 to 90% by mass, and particularly preferably from 70 to 90% by mass. When the content of the styrene-based monomer is less than 60% by mass, affinity of the styrene-based resin (c) to the quinacridone-based pigment (a) becomes insufficient and thus dispersion stability of the water-based pigment dispersion for ink-jet ink may be lowered. Also plain paper recording properties of the water-based ink for ink-jet recording composition obtained from water-based pigment dispersion may be lowered and the image recording density may be lowered and, furthermore, the water resistance may be lowered. When the total content of the styrene-based monomer unit is 95% by mass or less based on all monomer components, it is possible to prevent a risk of deterioration of a long-term stability or dispersion stability in water system because the content of the monomer units having an anionic group contributing to the dispersion can be ensured. On the other hand, when the content of the styrene-based monomer is within the above range, solubility of the styrene-based resin (c) in an aqueous medium can be improved and dispersibility and dispersion stability of the pigment in the water-based pigment dispersion for ink-jet ink can be improved. Furthermore, printing stability is improved when used as the water-based ink composition for ink-jet recording.

As the unsaturated aliphatic carboxylic acid having a radical polymerizable double bond to be copolymerized with the styrene-based monomer, known compounds can be used. Examples thereof include acrylic acid, methacrylic acid,  $\alpha$ -ethylacrylic acid, crotonic acid,  $\alpha$ -methylcrotonic acid,  $\alpha$ -ethylcrotonic acid, isocrotonic acid, maleic acid, fumaric acid, itaconic acid, citraconic acid, measaconic acid and glutaconic acid. Among these compounds, acrylic acid or methacrylic acid are preferably used, and the two are particularly preferably used in combination. By using acrylic acid in combination with methacrylic acid, copolymerizability on synthesis of the resin is improved and thus uniformity of the resin is improved. Consequently, there may be obtained a pigment dispersion which is excellent in storage stability and contains finely ground particles.

[0017]

As the monomer of the styrene-based resin (c) in the present invention, three kinds of monomers such as styrene-based monomer, acrylic acid and methacrylic acid are preferably used. The total content thereof is preferably 95% by mass or more based on all monomer components so as to enhance dispersibility and to obtain a high Tg.

[0018]

The styrene-based resin (c) used in the present invention preferably forms a coating on the surface of the

pigment stable in an aqueous medium, and preferably has stable water dispersibility in which an acidic group is neutralized by a basic compound. For this reason, an acid value of 50 to 300 is used. When the acid value is less than 50, hydrophilic property may become small, and dispersion stability may be lowered. On the other hand, when the acid value is more than 300, an aggregation of pigment is easily to occur, and the water resistance of printed articles using the ink composition may be lowered. An acid value is preferably is 60 to 250, and is more preferably 70 to 200.

[0019]

As the styrene-based resin (c), for example, known monomers other than the styrene-based monomer and the unsaturated aliphatic carboxylic acid having a radical polymerizable double bond can be used. Examples of the monomer include acrylate esters and methacrylate esters, such as methyl acrylate, methyl methacrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, sec-butyl acrylate, tert-butyl acrylate, 2-ethylbutyl acrylate, 1,3-dimethylbutyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, ethyl methacrylate, n-butyl methacrylate, 2-methylbutyl methacrylate, pentyl methacrylate, heptyl methacrylate and nonyl methacrylate; acrylate ester derivatives and methacrylate ester derivatives, such as 3-ethoxypropyl acrylate, 3-ethoxybutyl acrylate,

dimethylaminoethyl acrylate, 2-hydroxyethyl acrylate, 2-hydroxybutyl acrylate, ethyl- $\alpha$ -(hydroxymethyl) acrylate, dimethylaminoethyl methacrylate, hydroxyethyl methacrylate and hydroxypropyl methacrylate; acrylic acid aryl esters and acrylic acid aralkyl esters, such as phenyl acrylate, benzyl acrylate, phenylethyl acrylate and phenylethyl methacrylate; monoacrylate esters or monomethacrylate esters of polyhydric alcohol, such as diethylene glycol, triethylene glycol, polyethylene glycol, glycerin and bisphenol A; maleic acid dialkyl esters such as dimethyl maleate and diethyl maleate, and vinyl acetate. One or more kinds of these monomers can be added as a monomer component.

[0020]

As a method of producing the styrene-based resin (c), a conventional polymerization method can be employed and examples thereof include a method of polymerization reaction in the presence of a polymerization catalyst, for example, solution polymerization, suspension polymerization or bulk polymerization. Examples of the polymerization catalyst include 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobisisobutyronitrile, 1,1'-azobis(cyclohexane-1-carbonitrile), benzoyl peroxide, dibutyl peroxide and butylperoxy benzoate. The content is preferably from 0.1 to 10.0% by mass based on the vinyl monomer component.

[0021]

The weight-average molecular weight of the styrene-based resin (c) used in the present invention is within a range from 7,500 to 40,000, and more preferably from 7,500 to 30,000. The weight-average molecular weight is particularly preferably within a range from 10,000 to 25,000. When the weight-average molecular weight is less than 7,500, initial dispersion and reduction in particle size of the quinacridone-based pigment (a) can be easily conducted. However, long-term storage stability of the water-based pigment dispersion for ink-jet ink may be lowered and sedimentation due to aggregation of the pigment and the likes may occur. On the other hand, when the weight-average molecular weight of the styrene-based resin (c) is more than 40,000, the viscosity of the water-based ink composition for ink-jet recording prepared from the water-based pigment dispersion for ink-jet ink containing the same increases and ejection stability of the ink may be reduced.

[0022]

The glass transition point of the styrene-based resin (c) used in the present invention is preferably 90°C or higher, and is more preferably within a range from 100°C to 150°C. When the glass transition point is 90°C or higher, thermostability of the ink composition is improved. Therefore, even when the water-based ink for ink-jet recording composition prepared from the water-based pigment



dispersion is used for thermal jet type ink-jet recording, there may not arise a change in properties, which causes ink ejection failure due to repeated heating, and thus it is preferred.

The glass transition point of the styrene-based resin (c) in the present invention is measured by the differential scanning calorimetry.

[0023]

The styrene-based resin (c) used in the present invention may be a random copolymer or a graft copolymer. The graft copolymer includes, for example, a graft copolymer in which a copolymer of styrene and nonionic monomer copolymerizable with styrene or polystyrene constitutes a stem or branch, and a copolymer of acrylic acid, methacrylic acid and the other monomer including styrene constitutes a branch or stem. The styrene-based resin (c) may be a mixture of the graft copolymer and the random copolymer.

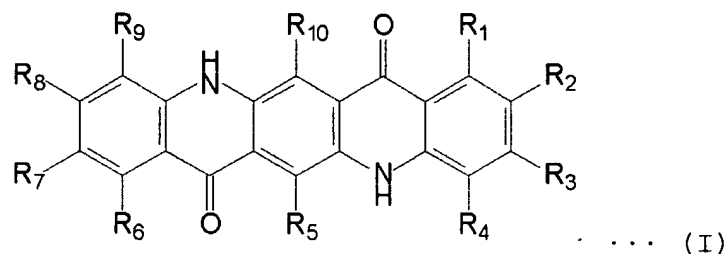
[0024]

As the alkali metal hydroxide (d) in the present invention, for example, sodium hydroxide, potassium hydroxide and lithium hydroxide can be used. Among these, potassium hydroxide is preferably used. The amount of the alkali metal hydroxide (d) is preferably 0.8 to 1.2 times the amount required to neutralize all carboxyl groups of the styrene-based resin (c).

[0025]

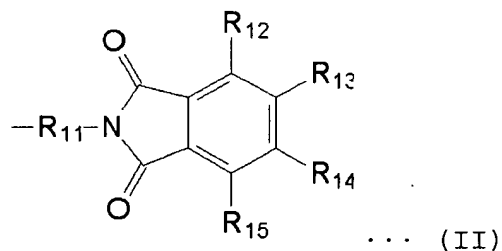
The compound (b) used in the present invention is represented by the formula (I):

[Chemical 7]



wherein  $R_1$  to  $R_{10}$  each independently represents hydrogen, fluorine, chlorine, bromine, iodine, a methyl group or an alkyl group having 2 to 8 carbon atoms, or a group represented by the formula (II):

[Chemical 8]

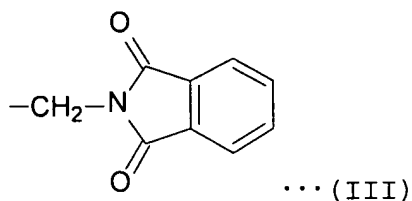


wherein  $R_{11}$  represents a methylene group or an alkylene group or alkenyl group having 2 to 8 carbon atoms, and  $R_{12}$  to  $R_{15}$  each independently represents hydrogen, fluorine, chlorine, bromine, iodine, a methyl group or an alkyl group having 2 to 8 carbon atoms, or phenyl group; and at least one of  $R_1$  to  $R_{10}$  is the group represented by the formula (II).

[0026]

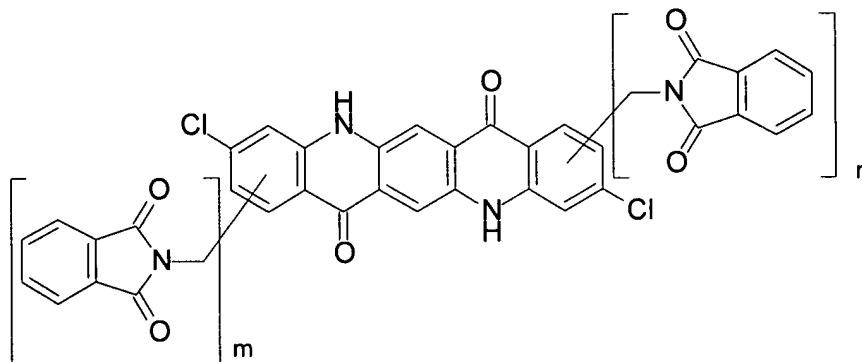
Specific examples of more preferred compounds among the compound (b) represented by the formula (I) include compounds represented by the following formula (IV) having a group represented by the following formula (III):

[Chemical 9]



[0027]

[Chemical 10]



... (IV)

wherein m and n each independently represents 0, 1, 2 or 3, provided that m and n are not simultaneously 0.

[0028]

The compound (b) represented by the formula (I) used in the present invention is preferably a compound having one or several groups represented by the formula (III) in the compound represented by the formula (IV) per molecule, and is

more preferably a compound having 1 to 2 groups represented by the formula (III) per molecule on average. The compound is particularly preferably a compound having 1 to 1.5 groups per molecule on average. When the number of the group represented by the formula (III) is less than 1 per molecule on average, the effect on dispersion stability may not be exerted. On the other hand, when the number of the group is more than 2 per molecule on average, characteristics of the ink composition for ink-jet recording may be reduced, for example, bleeding occurs.

[0029]

When the compound (b) represented by the formula (I) is a compound having groups represented by the formula (III), it can be synthesized by reacting non-substituted quinacridone, dimethylquinacridone or dichloroquinacridone with phthalimide and formaldehyde or paraformaldehyde in a concentrated sulfuric acid.

[0030]

In the present invention, the quinacridone-based pigment (a) does not include the compound (b).

In the present invention, the content of the compound (b) represented by the formula (I) is preferably from 1 to 20% by mass, and more preferably from 2 to 15% by mass, based on the total amount of the quinacridone-based pigment (a) and the compound represented by the formula (I). When the

content of the compound (b) represented by the formula (I) is less than 1% by mass, the effect of using in combination may be exerted with difficulty. On the other hand, when the content is more than 20% by mass, storage stability of the pigment dispersion for ink-jet ink and water-based ink composition for ink-jet recording may be drastically reduced.

[0031]

A colored kneaded mixture for ink-jet ink in the present invention is preferably produced by the following method.

That is, it is produced by the method comprising kneading a mixture containing the quinacridone-based pigment (a), the compound (b) represented by the formula (I), the styrene-based resin (c) and the alkali metal hydroxide (d) to prepare a colored kneaded mixture, and dispersing the colored kneaded mixture in an aqueous medium.

[0032]

When producing the colored kneaded mixture for ink-jet ink in the present invention, the mixture containing the quinacridone-based pigment (a), the compound (b) represented by the formula (I), the styrene-based resin (c) and the alkali metal hydroxide (d) may comprise a humectant. By comprising a humectant, it becomes easy to adjust the solid content of the mixture to the value suitable for kneader, and further, coating on the surface of the pigment rapidly

proceeds since the surface of the pigment becomes easy to get wet due to the humectant, and as the result, the humectant is replaced by the styrene-based resin. In addition, even if the humectant used in the process of producing the colored kneaded mixture remains in a water-based ink composition with a small amount, there is not an adverse effect because the humectant is fundamentally comprised as anti-drying agent in the water-based ink composition for ink-jet recording.

[0033]

As the humectant in the present invention, there can be used known humectants which have hitherto been used in the water-based ink for ink-jet recording. Examples of the humectant include polyols such as glycerin, ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, polyethylene glycol, propylene glycol, dipropylene glycol, polypropylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2,6-hexanetriol, trimethylolpropane and pentaerythritol; lactams such as 2-pyrrolidone, N-methyl-2-pyrrolidone and  $\epsilon$ -caprolactam; and 1,3-dimethylimidazolidinone.

[0034]

The humectant used in the kneading step preferably does not have strong solubility to the styrene-based resin, and preferably does not become a homogeneous solution when stirred with the styrene-based resin having a resin

concentration of 25% by mass. Further, when the humectant remains with an amount of 5% by mass or more in the water-based ink composition for ink-jet recording, it is preferably the one which does not deteriorate the properties of the water-based ink composition.

The amount of the humectant is within a range from 40 to 80 parts by mass based on 100 parts by mass of the quinacridone-based pigment (a). The amount of the humectant within said range is preferable since it is possible to make the solid components themselves into a blending condition with ease, and to apply a sufficient shearing force during the kneading step.

[0035]

In the production method, the amount of the alkali metal hydroxide (d) is 0.8 to 1.2 times the amount required to neutralize all carboxyl groups of the styrene-based resin (c). When the styrene-based resin is kneaded together with the quinacridone-based pigment (a), the alkali metal hydroxide (d) and the compound (b) represented by the formula (I), it is preferable to knead under high shearing force. By kneading them under high shearing force, the quinacridone-based pigment (a) is finely crushed, and further the adsorption of the styrene-based resin (c) on the surface of the particles proceeds to obtain a homogeneous colored kneaded mixture for ink-jet ink.

[0036]

The alkali metal hydroxide (d) is added as an aqueous solution or an organic solvent solution of the alkali metal hydroxide (d). In this case, the content of the aqueous solution or organic solvent solution of the alkali metal hydroxide (d) is preferably from 20% to 50% by mass. As the organic solvent which dissolves the alkali metal hydroxide (d), alcohol solvents such as methanol, ethanol and isopropanol are preferably used. Particularly, an aqueous solution of the alkali metal hydroxide (d) is preferably used in the present invention.

[0037]

The concentration of the solid content in the colored kneaded mixture for ink-jet ink during a kneading step, is preferably 50 to 80% by mass. By carrying out a kneading step, while keeping the concentration of the solid content within said range, it is possible to apply a sufficient shearing force. Further, the quinacridone-based pigment (a) can be crushed enough to obtain a homogeneous colored kneaded mixture for ink-jet ink.

Considering the temperature properties of the styrene-based resin (c), the temperature during a kneading step can be adequately controlled to apply a sufficient shearing force to the mixture. However, it is preferable to carry within the range that the temperature during a kneading step is



lower than the glass transition point of the styrene-based resin (c) and the difference of the temperature between the temperature during a kneading step and said glass transition point is smaller than 50°C. By carrying out the kneading within said temperature range, problems that the shearing force is not sufficient due to lowered viscosity of the mixture accompanying an increase of kneading temperature and the dispersion of the kneaded mixture after finish of kneading becomes difficult due to the difficulty of increase of the concentration of the solid content, may not happen.

[0038]

When the colored kneaded mixture for ink-jet ink is produced, the kneader having stirring tank is preferably used than the open-type kneader not having stirring tank such as two-roll. If such kneader is used, it is possible to dilute the colored kneaded mixture for ink-jet ink after kneading directly in an aqueous medium and as a result, to produce a water-based pigment dispersion for ink-jet ink. Examples of the kneader having stirring tank preferably include a planetary mixer. Comparing the planetary mixer with other two-roll and the like, since it is possible to carry out the kneading treatment within a wide range of viscosity, and further adding an aqueous medium and elimination by distillation under reduced pressure is possible, it is easy to control the viscosity and the shearing force applied

during the kneading step.

[0039]

The colored kneaded mixture for ink-jet ink following kneading obtained by diluting with an aqueous medium is preferably further subject to a dispersion treatment by the disperser. By subjecting to the dispersion treatment, coarse dispersed particles in the water-based pigment dispersion for ink-jet ink are further ground and the particle size of dispersed particles are diminished, and thus ink-jet characteristics such as ejection stability and print density of the water-based ink composition for ink-jet recording are more improved.

[0040]

As the disperser used in the dispersion treatment, a well known disperser may be used, and examples of the disperser include ultrasonic homogenizer, high-pressure homogenizer, paint shaker, ball mill, roll mill, sand mill, sand grinder, Dinomill, Dispermat, Nano mill, SC mill and nanomizer. Among them, one or a combination of at least two dispersers may be used.

[0041]

The aqueous medium used in the case of diluting the colored kneaded mixture for ink-jet ink may contain a humectant because it is necessary to prevent drying of the water-based pigment dispersion for ink-jet ink and to adjust

the viscosity when a dispersion treatment is carried out. The total content of the humectant used in the case of diluting the colored kneaded mixture and that contained in the colored kneaded mixture for ink-jet ink is preferably 3 to 50% by mass, and more preferably from 5 to 40% by mass, based on the water-based pigment dispersion for ink-jet ink. When the content is less than the lower limit, the effect of inhibiting drying may be lowered. On the other hand, when the content is more than the upper limit, dispersion stability of the dispersion may be lowered. The humectant used to prepare the colored kneaded mixture for ink-jet ink and the humectant contained in the aqueous medium which is used to dilute the colored kneaded mixture may be the same or different.

[0042]

The water-based ink composition for ink-jet recording using the colored kneaded mixture for ink-jet ink of the present invention can be prepared by conventional method. In the case of preparing the water-based ink composition for ink-jet recording, since crude particles cause nozzle clogging and the likes that deteriorate the properties of print, the crude particles may be removed by centrifugation or filtering treatment after the preparation of ink.

[0043]

In the case of preparing the water-based ink

composition for ink-jet recording using the pigment dispersion for ink-jet ink of the present invention, in order to inhibit drying of ink, afore-mentioned humectant may be added. The content of the humectant used for the purpose inhibiting drying is preferably from 3 to 50% by mass based on the ink.

[0044]

In the case of preparing the water-based ink composition for ink-jet recording using the pigment dispersion for ink-jet ink of the present invention, penetrants can be added for the purpose of improving permeability to the medium to be recorded and adjusting dot size on a recording medium.

Examples of the penetrant include lower alcohols such as ethanol and isopropyl alcohol; ethylene oxide adducts of alkyl alcohol, such as ethylene glycol hexyl ether and diethylene glycol butyl ether; and propylene oxide adducts of alkyl alcohol, such as propylene glycol propyl ether. The content of the penetrant is preferably from 0.01 to 10% by mass based on the ink.

[0045]

In the case of preparing the water-based ink composition for ink-jet recording using the pigment dispersion for ink-jet ink of the present invention, surfactants can be added so as to adjust ink properties such

as surface tension. Examples of the surfactant include, but are not limited to, various anionic surfactants, nonionic surfactants, cationic surfactants and amphoteric surfactants. Among these surfactants, anionic surfactants and nonionic surfactants are preferable.

[0046]

Examples of the anionic surfactant include alkylbenzenesulfonic acid salt, alkylphenylsulfonic acid salt, alkylnaphthalenesulfonic acid salt, higher fatty acid salt, sulfate ester salt of higher fatty acid ester, sulfonic acid salt of higher fatty acid ester, sulfate ester salt and sulfonic acid salt of higher alcohol ether, higher alkyl sulfosuccinic acid salt, polyoxyethylene alkyl ether carboxylic acid salt, polyoxyethylene alkyl ether sulfuric acid salt, alkyl phosphoric acid salt and polyoxyethylene alkyl ether phosphoric acid salt. Specific examples thereof include dodecylbenzenesulfonic acid salt, isopropylnaphthalenesulfonic acid salt, monobutylphenylphenolmonosulfonic acid salt, monobutylbiphenylsulfonic acid salt and dibutylphenylphenoldisulfonic acid salt.

[0047]

Examples of the nonionic surfactant include polyoxyethylene alkyl ether, polyoxyethylene alkyl phenyl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid

ester, polyoxyethylene sorbitan fatty acid ester, polyoxyethylene sorbitol fatty acid ester, glycerin fatty acid ester, polyoxyethylene glycerin fatty acid ester, polyglycerin fatty acid ester, sucrose fatty acid ester, polyoxyethylene alkylamine, polyoxyethylene fatty acid amide, fatty acid alkyloamide, alkyl alkanolamide, acetylene glycol, oxyethylene adduct of acetylene glycol and polyethylene glycol-polypropylene glycol block copolymer. Among these surfactants, polyoxyethylene nonyl phenyl ether, polyoxyethylene octyl phenyl ether, polyoxyethylene dodecyl phenyl ether, polyoxyethylene alkyl ether, polyoxyethylene fatty acid ester, sorbitan fatty acid ester, polyoxyethylene sorbitan fatty acid ester, fatty acid alkylolamide, acetylene glycol, oxyethylene adduct of acetylene glycol and polyethylene glycol-polypropylene glycol block copolymer are preferable.

[0048]

As the other surfactant, for example, there can be used silicone-based surfactants such as polysiloxaneoxyethylene adduct; fluorine surfactants such as perfluoroalkylcarboxylic acid salt, perfluoroalkylsulfonic acid salt and oxyethylene perfluoroalkyl ether; and biosurfactants such as spiculisporic acid, rhamnolipid and lysolecithin. These surfactants can be used alone or in combination. Taking account of dissolution stability of the surfactant, HLB is

preferably within a range from 7 to 20.

When the surfactant is added, the content is preferably within a range from 0.001 to 1% by mass, more preferably from 0.001 to 0.5% by mass, and most preferably from 0.01 to 0.2% by mass, based on the entire mass of the ink composition for ink-jet recording. When the content of the surfactant is less than 0.001% by mass, the effect of adding the surfactant may not be exerted. On the other hand, when the content is more than 1% by mass, there may cause problems such as bleeding.

[0049]

In the case of preparing the water-based ink composition for ink-jet recording using the water-based pigment dispersion for ink-jet ink of the present invention, antiseptics, viscosity adjustors, pH adjustors, chelating agents, plasticizers, antioxidants and ultraviolet absorbers can be added, if necessary.

[0050]

The amount of a quinacridone-based pigment (a) in a pigment dispersion for ink-jet ink of the present invention is preferably 5 to 25% by mass, and is more preferably 5 to 20% by mass. When the content of the quinacridone-based pigment (a) is less than 5% by mass, coloration of the water-based ink composition for ink-jet recording prepared from the pigment dispersion for ink-jet ink of the present invention

is not sufficient, and a sufficient print concentration is not obtained. On the other hand, the content of the quinacridone-based pigment (a) is more than 25% by mass, the dispersion stability of the pigment in the pigment dispersion for ink-jet ink tends to decrease.

[0051]

In order to obtain a sufficient print concentration and to secure the dispersion stability of dispersing particles in the ink, the amount of a quinacridone-based pigment (a) in a water-based ink composition for ink-jet recording prepared from the pigment dispersion for ink-jet ink of the present invention is preferably 2 to 10% by mass.

[0052]

The water-based ink composition for ink-jet recording can be preferably used as an ink for ink-jet recording. Examples of the ink-jet system to which the ink composition is applied include, but are not limited to, known systems, for example, continuous systems such as charge control type system and spray type system; and drop on-demand type systems such as piezo type system, thermal type system and electrostatic attraction type system.

[0053]

[Examples]

The present invention will now be described in detail by way of examples. In the examples, parts and percentages



are by mass unless otherwise specified. Resins A to C used in the examples are as follows.

[0054]

Resin A: resin including monomers in a ratio of styrene/acrylic acid/methacrylic acid = 77/10/13 (mass ratio) having a weight-average molecular weight of 7700, an acid value of 151 mgKOH/g and a glass transition point of 107°C

Resin B: resin including monomers in a ratio of styrene/acrylic acid/methacrylic acid = 77/10/13 (mass ratio) having a weight-average molecular weight of 11000, an acid value of 152 mgKOH/g and a glass transition point of 118°C

Resin C: resin including monomers in a ratio of styrene/acrylic acid/methacrylic acid = 77/10/13 (mass ratio) having a weight-average molecular weight of 20000, an acid value of 151 mgKOH/g and a glass transition point of 107°C

Resin D: resin including monomers in a ratio of styrene/methacrylic acid = 77/23 (mass ratio) having a weight-average molecular weight of 10700, an acid value of 146 mgKOH/g and a glass transition point of 121°C

Resin E: resin including monomers in a ratio of styrene/acrylic acid/methacrylic acid = 77/10/13 (mass ratio) having a weight-average molecular weight of 5000, an acid value of 150 mgKOH/g and a glass transition point of 105°C

Resin F: resin including monomers in a ratio of styrene/acrylic acid/methacrylic acid = 77/10/13 (mass ratio)

having a weight-average molecular weight 45000, an acid value of 153 mgKOH/g and a glass transition point of 128°C

Resin G: resin including monomers in a ratio of styrene/methyl methacrylate/acrylic acid/methacrylic acid = 50/22/10/13 (mass ratio) having a weight-average molecular weight of 12000, an acid value of 149 mgKOH/g and a glass transition point of 118°C

[0055]

As used herein, the weight-average molecular weight is a value, as measured by a GPC (gel permeation chromatography) method, reduced in terms of a molecular mass of polystyrene used as a certified reference substance.

The measurement was carried out by the following apparatus and conditions.

Delivery pump: LC-9A

System controller: SIL-6B

Auto-injector: SIL-6B

Detector: RID-6A

The above are those manufactured by Shimadzu Corporation.

Data processing software: Sic480II Data Station (manufactured by System Instruments Co., Ltd.)

Column: GL-R400 (Gard Column) + GL-R440 + GL-R450 + GL-R400M (manufactured by Hitachi Chemical Co., Ltd.)

Eluent: THF

Flow rate: 2 ml/min

Column temperature: 35°C

[0056]

(Example 1)

A mixture with the following composition was charged in a planetary mixer PLM-V-50V (manufactured by Inoue Seisakusho) having a volume of 50 L and, after heating a jacket, the mixture was kneaded at a low speed (rotation speed: 21 rpm, revolution speed: 14 rpm) until the temperature of contents reached 60°C. After changing to high speed (rotation speed: 35 rpm, revolution speed: 24 rpm), kneading was continued.

Resin A	750 g
Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)	4625 g
Phthalimidomethylated 3,10-dichloroquinacridone (average number of phthalimidemethyl group per molecule: 1.4)	375 g
DEG	2700 g
Aqueous 34% by mass potassium hydroxide solution	333 g
Ion-exchanged water	200 g

[0057]

On changing to high speed, a current value of a planetary mixer was 5 A. After kneading was continued, a

maximum current value of the planetary mixer was 15 A. After kneading was continued for one hour since the maximum current value was attained, the current value of the planetary mixer was 10 A. To the resulting kneaded mixture in a stirring tank, 200 g of ion-exchanged water was added and kneading was continued. Uniform mixing was confirmed and, after an additional one hour, 200 g of ion-exchanged water was added, followed by uniform mixing and further continuous kneading.

[0058]

Kneading was continued for 4 hours since the observation of the maximum current value to obtain a colored resin kneaded mixture. To the resulting colored kneaded mixture, 6400 g of ion-exchanged water was added in several portions over 2 hours while stirring using a planetary mixer.

After adding ion-exchanged water, the colored kneaded mixture following diluting with water is taken from the planetary mixer. The solid content of the colored kneaded mixture after diluting with water was 39.0% by mass. To 12 kg of the colored kneaded mixture taken after diluting with water, 5.83 kg of diethylene glycol and 5.57 kg of ion-exchanged water were added by several portions while stirring using a dispersion stirrer to obtain a water-based pigment dispersion precursor.

18 kg of the water-based pigment dispersion precursor was dispersed by using a bead mill (Nano Mill NM-G2L;

manufactured by ASADA IRON WORKS CO., LTD.) under the following conditions to obtain a pigment dispersion A-1.

[0059]

Dispersion conditions

Disperser: Nano millNM-G2L (manufactured by ASADA IRON WORKS CO., LTD.)

Beads: 0.3 mm in diameter zirconia beads

Amount of beads filled: 85%

Cooling water temperature: 10°C

Rotation speed: 2660 rpm

(Disk peripheral speed: 12.5 m/sec)

Delivery amount: 200 g/10 sec

A dispersion treatment was conducted while circulating for one hour under the above conditions. The content of the quinacridone-based pigment of the pigment dispersion A-1 was 15.8% by mass.

[0060]

(Example 2)

A mixture with the following composition was charged in a planetary mixer having a volume of 50 L and kneading was carried out in the same manner as in Example 1.

Resin B 750 g

Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS

(manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)

4630 g

Phthalimidomethylated 3,10-dichloroquinacridone (average  
number of phthalimidemethyl group per molecule: 1.4)

380 g

DEG

2900 g

Aqueous 34% by mass potassium hydroxide solution

335 g

On changing to high speed, a current value of a planetary mixer was 5 A. After kneading was continued, a maximum current value of the planetary mixer was 15 A. After kneading was continued for 4 hours while adding ion-exchanged water every 30 minutes since the maximum current value was attained, a colored kneaded mixture was obtained. During this period, the current value of the planetary mixer was 12 A. To the resulting colored kneaded mixture in the stirring bath, 6200 g of ion-exchanged water was added in several portions over 2 hours while kneading.

[0061]

After adding ion-exchanged water, the colored kneaded mixture following diluting with water is taken from the planetary mixer. The solid content of the colored kneaded mixture after diluting with water was 39.9 % by mass. To 12 kg of the colored kneaded mixture taken after diluting with water, 5.81 kg of diethylene glycol and 6.15 kg of ion-exchanged water were added by several portions while stirring using a dispersion stirrer to obtain a water-based pigment

dispersion precursor.

18 kg of the water-based pigment dispersion precursor was dispersed by using a bead mill (Nano Mill NM-G2L; manufactured by ASADA IRON WORKS CO., LTD.) in the same manner as in Example 1 except the delivery amount being 185 g/10 sec. The content of the quinacridone-based pigment of the pigment dispersion B-1 was 15.8% by mass.

[0062]

(Example 3)

A mixture with the following composition was charged in a planetary mixer having a volume of 50 L and kneading was carried out in the same manner as in Example 1.

[0063]

Resin B	750 g
Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)	4630 g
Phthalimidomethylated 3,10-dichloroquinacridone (average number of phthalimidemethyl group per molecule: 1.4)	380 g
DEG	3000 g
Aqueous 34% by mass potassium hydroxide solution	335 g

On changing to high speed, a current value of a planetary mixer was 5 A. After kneading was continued, a

maximum current value of the planetary mixer was 15 A. After kneading was continued for 2 hours since the maximum current value was attained, the current value of the planetary mixer was 10 A. To the resulting kneaded mixture in the stirring bath, 200 g of ion-exchanged water heated to 60°C was slowly added while kneading.

[0064]

After kneading was continued for 4 hours since the maximum current value was attained, a colored kneaded mixture was obtained. To the resulting colored kneaded mixture, total 6800 g of ion-exchanged water heated to 60°C was added in several portions over 2 hours while stirring by the planetary mixer.

[0065]

After adding ion-exchanged water, the colored kneaded mixture following diluting with water is taken from the planetary mixer. The solid content of the colored kneaded mixture after diluting with water was 37.6 % by mass. To 12 kg of the colored kneaded mixture taken after diluting with water and 10.58 kg of ion-exchanged water were added by several portions while stirring using a dispersion stirrer to obtain a water-based pigment dispersion precursor.

18 kg of the water-based pigment dispersion precursor was dispersed by using a bead mill (Nano Mill NM-G2L; manufactured by ASADA IRON WORKS CO., LTD.) in the same



manner as in Example 1 except the delivery amount being 190 g/10 sec, and the pigment dispersion C-1 was obtained. The content of the quinacridone-based pigment of the pigment dispersion C-1 was 15.8% by mass.

[0066]

(Example 4)

A mixture with the following composition was charged in a planetary mixer having a volume of 50 L and kneading was carried out in the same manner as in Example 1.

[0067]

Resin C	1000 g
Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)	
	4750 g
Phthalimidomethylated 3,10-dichloroquinacridone (average number of phthalimidemethyl group per molecule: 1.4)	
	250 g
DEG	3200 g
Aqueous 34% by mass potassium hydroxide solution	
	489 g

[0068]

On changing to high speed, a current value of a planetary mixer was 5 A. After kneading was continued, a maximum current value of the planetary mixer was 15 A. After kneading was continued for 2 hours since the maximum current

value was attained, the current value of the planetary mixer was 10 A. To the resulting kneaded mixture in the stirring bath, 300 g of ion-exchanged water heated to 60°C was slowly added while kneading.

[0069]

After kneading was continued for 4 hours since the maximum current value was attained, a colored kneaded mixture was obtained. To the resulting colored kneaded mixture, total 6700 g of ion-exchanged water heated to 60°C was added in several portions over 2 hours while stirring by the planetary mixer.

[0070]

After adding ion-exchanged water, the colored kneaded mixture following diluting with water is taken from the planetary mixer. The solid content of the colored kneaded mixture after diluting with water was 38.5% by mass. To 12 kg of the colored kneaded mixture taken after diluting with water, 1.35 kg of diethylene glycol and 9.75 kg of ion-exchanged water were added by several portions while stirring using a dispersion stirrer to obtain a water-based pigment dispersion precursor.

18 kg of the water-based pigment dispersion precursor was dispersed by using a bead mill (Nano Mill NM-G2L; manufactured by ASADA IRON WORKS CO., LTD.) in the same manner as in Example 1 except the delivery amount being 190

g/10 sec, and the pigment dispersion D-1 was obtained. The content of the quinacridone-based pigment of the pigment dispersion D-1 was 15.4% by mass.

[0071]

(Example 5)

A mixture with the following composition was charged in a planetary mixer having a volume of 50 L and kneading was carried out in the same manner as in Example 1.

Resin D	750 g
Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)	4630 g
Phthalimidomethylated 3,10-dichloroquinacridone (average number of phthalimidemethyl group per molecule: 1.4)	380 g
DEG	3100 g
Aqueous 34% by mass potassium hydroxide solution	322 g

[0072]

On changing to high speed, a current value of a planetary mixer was 5 A. After kneading was continued, a maximum current value of the planetary mixer was 15 A. After kneading was continued for 2 hours since the maximum current value was attained, the current value of the planetary mixer was 12 A. To the resulting kneaded mixture in the stirring

bath, 300 g of ion-exchanged water heated to 60°C was slowly added while kneading.

[0073]

After kneading was continued for 4 hours since the maximum current value was attained, a colored kneaded mixture was obtained. To the resulting colored kneaded mixture, total 6700 g of ion-exchanged water heated to 60°C was added in several portions over 2 hours while stirring by the planetary mixer.

After adding ion-exchanged water, the colored kneaded mixture following diluting with water is taken from the planetary mixer. The solid content of the colored kneaded mixture after diluting with water was 38.1 % by mass. To 12 kg of the colored kneaded mixture taken after diluting with water, 1.49 kg of diethylene glycol and 9.34 kg of ion-exchanged water were added by several portions while stirring using a dispersion stirrer to obtain a water-based pigment dispersion precursor.

18 kg of the water-based pigment dispersion precursor was dispersed by using a bead mill in the same manner as in Example 1 except the delivery amount being 195 g/10 sec, and the pigment dispersion E-1 was obtained. The content of the quinacridone-based pigment of the pigment dispersion E-1 was 15.8% by mass.

[0074]

(Comparative Example 1)

A mixture with the following composition was charged in a planetary mixer having a volume of 50 L and kneading was carried out in the same manner as in Example 1.

[0075]

Resin B	1000 g
Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)	
	5000 g
DEG	3200 g
Aqueous 34% by mass potassium hydroxide solution	
	447 g

[0076]

On changing to high speed, a current value of a planetary mixer was 5 A. After kneading was continued, a maximum current value of the planetary mixer was 10 A. After kneading was continued for 2 hours since the maximum current value was attained, the current value of the planetary mixer was 8 A. To the resulting kneaded mixture in the stirring bath, 200 g of ion-exchanged water heated to 60°C was slowly added while kneading.

[0077]

After kneading was continued for 4 hours since the maximum current value was attained, a colored kneaded mixture was obtained. To the resulting colored kneaded mixture,

total 6000 g of ion-exchanged water heated to 60°C was added in several portions over 2 hours while stirring by the planetary mixer.

After adding ion-exchanged water, the colored kneaded mixture following diluting with water is taken from the planetary mixer. The solid content of the colored kneaded mixture after diluting with water was 40.4 % by mass. To 12 kg of the colored kneaded mixture taken after diluting with water, 1.42 kg of diethylene glycol and 11.25 kg of ion-exchanged water were added by several portions while stirring using a dispersion stirrer to obtain a water-based pigment dispersion precursor.

18 kg of the water-based pigment dispersion precursor was dispersed by using a bead mill in the same manner as in Example 1 except the delivery amount being 195 g/10 sec, and the pigment dispersion F-1 was obtained.

[0078]

The content of the quinacridone-based pigment of the pigment dispersion F-1 was 16.0% by mass.

[0079] (Comparative Example 2)

Preparation of aqueous resin solution

In accordance with the following formulation, a methyl ethyl ketone solution of a resin B was prepared.

Methyl ethyl ketone (abbreviated as MEK) 50 g

Resin B

50 g

To this was added a mixed solution of 247.6 g of ion-exchanged water and 22.35 g of an aqueous 34% by mass potassium hydroxide solution, followed by sufficient stirring to obtain a resin B solution.

MEK with water were distilled off from the resin B solution under reduced pressure condition of a water bath temperature of 35°C and a pressure of 20 hPa. After the completion of distillation of MEK, ion-exchanged water was added to obtain an aqueous resin B solution having a solid content of 20% by mass.

#### Dispersion of pigment

In a 250 ml polyethylene bottle, 400 g of 1.2 mm in diameter zirconia beads were placed and the following components were treated by a paint conditioner manufactured by Toyo Seiki Seisaku-Sho, Ltd. for 4 hours.

Aqueous resin B solution	8.64 g
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Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS (manufactured by DAINIPPON INK AND CHEMICALS, INC.)	
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	9.25 g
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Phthalimidomethylated 3,10-dichloroquinacridone (average number of phthalimidemethyl group per molecule: 1.4)	
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	0.75 g
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DEG	20.0 g
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Ion-exchanged water	20.0 g
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After the completion of the treatment, 10.33 g of ion-

exchanged water was added. After further treating for 30 minutes, beads were removed by filtration to obtain a pigment dispersion G-1.

The content of the quinacridone-based pigment of the pigment dispersion G-1 was 13.4% by mass.

[0080]

(Comparative Example 3)

A mixture with the following composition was charged in a planetary mixer having a volume of 50 L and kneading was carried out in the same manner as in Example 1.

Resin E	750 g
Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)	4700 g
Phthalimidomethylated 3,10-dichloroquinacridone (average number of phthalimidemethyl group per molecule: 1.4)	300 g
DEG	2500 g
Aqueous 34% by mass potassium hydroxide solution	331 g

[0081]

On changing to high speed, a current value of a planetary mixer was 5 A. After kneading was continued, a maximum current value of the planetary mixer was 12 A. After kneading was continued for 2 hours since the maximum current



value was attained, the current value of the planetary mixer was 10 A. To the resulting kneaded mixture in a stirring tank, 200 g of ion-exchanged water heated to 60°C was slowly added and kneading was continued.

Kneading was continued for 4 hours since the observation of the maximum current value to obtain a colored kneaded mixture. To the resulting colored kneaded mixture, 6800 g of ion-exchanged water heated to 60°C was added in several portions over 2 hours while stirring using a planetary mixer.

[0082]

After adding ion-exchanged water, the colored kneaded mixture following diluting with water is taken from the planetary mixer. The solid content of the colored kneaded mixture after diluting with water was 39.0% by mass. To 12 kg of the colored kneaded mixture taken after diluting with water, 2.00 kg of diethylene glycol and 9.40 kg of ion-exchanged water were added by several portions while stirring using a dispersion stirrer to obtain a water-based pigment dispersion precursor.

18 kg of the water-based pigment dispersion precursor was dispersed by using a bead mill in the same manner as in Example 1 to obtain a pigment dispersion H-1. The content of the quinacridone-based pigment of the pigment dispersion H-1 was 16.0% by mass.

[0083]

(Comparative Example 4)

A mixture with the following composition was charged in a planetary mixer having a volume of 50 L and kneading was carried out in the same manner as in Example 1.

[0084]

Resin F	750 g
Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)	4630 g
Phthalimidomethylated 3,10-dichloroquinacridone (average number of phthalimidemethyl group per molecule: 1.4)	380 g
DEG	3300 g
Aqueous 34% by mass potassium hydroxide solution	338 g
Ion-exchanged water	200 g

[0085]

On changing to high speed, a current value of a planetary mixer was 5 A. After kneading was continued, a maximum current value of the planetary mixer was 15 A. After kneading was continued for one hour since the maximum current value was attained, the current value of the planetary mixer was 13 A. To the resulting kneaded mixture in a stirring tank, 200 g of ion-exchanged water was added and kneading was

continued. Uniform mixing was confirmed and, after an additional one hour, 200 g of ion-exchanged water was added, followed by uniform mixing and further continuous kneading.

[0086]

Kneading was continued for 4 hours since the observation of the maximum current value to obtain a colored kneaded mixture. To the resulting colored kneaded mixture, 6400 g of ion-exchanged water was added in several portions over 2 hours while stirring using a planetary mixer.

After adding ion-exchanged water, the colored kneaded mixture following diluting with water is taken from the planetary mixer. The solid content of the colored kneaded mixture after diluting with water was 38.4 % by mass. To 12 kg of the colored kneaded mixture taken after diluting with water, 1.34 kg of diethylene glycol and 9.70 kg of ion-exchanged water were added by several portions while stirring using a dispersion stirrer to obtain a water-based pigment dispersion precursor.

18 kg of the water-based pigment dispersion precursor was dispersed by using a bead mill in the same manner as in Example 1 except the delivery amount being 195 g/10 sec to obtain a pigment dispersion I-1. The content of the quinacridone-based pigment of the pigment dispersion I-1 was 15.8 % by mass.

[0087]

(Comparative Example 5)

A mixture with the following composition was charged in a planetary mixer having a volume of 50 L and dispersion was carried out in the same manner as in Example 1.

Resin G	750 g
Quinacridone-based pigment: FASTOGEN SUPER MAGENTA RTS (manufactured by DAINIPPON INK AND CHEMICALS, INCORPORATED)	4630 g
Phthalimidomethylated 3,10-dichloroquinacridone (average number of phthalimidemethyl group per molecule: 1.4)	380 g
DEG	3000 g
Aqueous 34% by mass potassium hydroxide solution	329 g

On changing to high speed, a current value of a planetary mixer was 5 A. After kneading was continued, a maximum current value of the planetary mixer was 15 A. After kneading was continued for one hour since the maximum current value was attained, the current value of the planetary mixer was 13 A. To the resulting kneaded mixture in a stirring tank, 300 g of ion-exchanged water was added and kneading was continued. Uniform mixing was confirmed and, after an additional one hour, 200 g of ion-exchanged water was added, followed by uniform mixing and further continuous kneading.

[0088]

Kneading was continued for 4 hours since the observation of the maximum current value to obtain a colored kneaded mixture. To the resulting colored kneaded mixture, 6500 g of ion-exchanged water was added in several portions over 2 hours while stirring using a planetary mixer.

After adding ion-exchanged water, the colored kneaded mixture following diluting with water is taken from the planetary mixer. The solid content of the colored kneaded mixture after diluting with water was 39.5% by mass. To 12 kg of the colored kneaded mixture taken after diluting with water, 1.62 kg of diethylene glycol and 10.08 kg of ion-exchanged water were added by several portions while stirring using a dispersion stirrer to obtain a water-based pigment dispersion precursor.

18 kg of the water-based pigment dispersion precursor was dispersed by using a bead mill in the same manner as in Example 1 except the delivery amount being 195 g/10 sec to obtain a pigment dispersion J-1. The content of the quinacridone-based pigment of the pigment dispersion J-1 was 15.8% by mass. [0089]

(Evaluation of water-based pigment dispersion)

With respect to the water-based pigment dispersions thus obtained in the Examples and Comparative Examples, the particle size was measured at a cell temperature of 25°C by using a Microtrac UPA particle size analyzer (manufactured by

Leeds & Northrup Co). In that case, samples for measurement of the particle size were prepared by diluting each of the resulting water-based pigment dispersions with ion-exchanged water so as to adjust the content of the quinacridone-based pigment to 12.5%, and further diluting with ion-exchanged water by 500 times. The results are shown in Table 1.

[0090]

(Evaluation of dispersion stability)

In the same manner as in the case of the dispersion, the water-based pigment dispersions of the Examples and Comparative Examples were adjusted with ion-exchanged water after diluting with ion-exchanged water so as to adjust the content of the pigment to 12.5% by mass. After controlling the content of the pigment, the dispersion was sealed in a glassware such as screw-thread glass vial and subjected to a heating test in a thermostatic chamber at 60°C for one week. The dispersion stability was evaluated by observing a change in particle size before and after the heating test. The results are shown in Table 1.

[0091]

Table 1

	Dispersion	Volume-average particle size (nm)	Volume-average particle size after heating test (nm)	Change ratio
Example 1	A-1	108	112	4%
Example 2	B-1	106	103	-3%
Example 3	C-1	115	113	-2%
Example 4	D-1	116	116	0%
Example 5	E-1	125	134	7%
Comparative Example 1	F-1	127	142	12%
Comparative Example 2	G-1	137	145	6%
Comparative Example 3	H-1	107	116	8%
Comparative Example 4	I-1	118	115	-3%
Comparative Example 5	J-1	115	117	2%

[0092]

As shown in Table 1, in the water-based pigment dispersion obtained by the present invention, the initial particle size is small, and further the change ratio of the particle size after heating test is small. That is, accordingly to the present invention, the water-based pigment dispersion having more particulate pigment is obtained, and further the water-based pigment dispersant has excellent dispersion stability.

[0093]

(Preparation of ink composition)

A ion-exchanged water was added to the water-based pigment dispersion obtained by each examples and comparative examples, and 50.0 g of diluted water-based pigment solution

having 10 % by mass of quinacridone-based pigment was prepared. An ink composition in which it has the following composition and the content of quinacridone-based pigment in the composition is 5 % by mass, was prepared by using the diluted water-based pigment solution. Diluted water-based pigment solution

50.0 g
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2-pyrrolidinone 8.0 g

Triethylene glycol monobutyl ether 8.0 g

Glycerin	3.0 g
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SURFYNOL 465 (Surfactant manufactured by Air Products Co.,  
Ltd.) 0.5 g

Ion-exchanged water	30.5 g
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[0094] (Stability test of ink composition)

The resulting ink composition was sealed in a glassware such as screw-thread glass vial and subjected to a heating test in a thermostatic chamber at 70°C for one week. The stability of the ink composition was evaluated by observing a change in particle size and viscosity before and after the heating test.

The particle size was measured in the same manner as in the case of evaluation of the water-based pigment dispersion, except that the ink composition was diluted with ion-exchanged water by 100 times. The viscosity was measured by an E-type viscometer (VISCOMETER TV-20 manufactured by Tokyo Keiki Co., Ltd.) at 25°C.



The results are shown in Table 2.

[0095]

(Evaluation of ink-jet recordability)

The resulting ink composition before subjecting to the heating test was injected in a black pen of a thermal jet type DeskJet957C manufactured by Hewlett-Packard Co., Ltd., and then the printing test was carried out. Specifically, solid printing and fine-line printing were carried out using A4-size paper and the ejection state of the ink was observed. The results are shown in Table 2.

[0096]

Table 2

	Dispersion in use	Volume- average particle size before heating test (nm)	Volume- average particle size after heating test (nm)	Change ratio of particle size
Example 1	A-1	102	108	6%
Example 2	B-1	99	101	2%
Example 3	C-1	111	108	-3%
Example 4	D-1	107	108	1%
Example 5	E-1	121	128	6%
Comparative Example 1	F-1	125	243	94%
Comparative Example 2	G-1	129	215	67%
Comparative Example 3	H-1	111	122	10%
Comparative Example 4	I-1	118	118	0%
Comparative Example 5	J-1	115	118	3%

Table 2 (continued)

	Viscosity before heating test (mPa·s)	Viscosity after heating test (mPa·s)	Change ratio of viscosity	Evaluation of Ink-jet recordability
Example 1	3.15	3.24	3%	◎
Example 2	3.26	3.32	2%	◎
Example 3	2.78	2.65	-5%	◎
Example 4	3.22	3.21	0%	◎
Example 5	3.18	3.2	1%	○
Comparative Example 1	2.97	4.85	63%	×
Comparative Example 2	3.42	7.77	127%	△
Comparative Example 3	2.81	3.24	15%	○
Comparative Example 4	4.12	4.02	-2%	××
Comparative Example 5	3.01	3.05	1%	△

[0097]

With respect to evaluation of ink-jet recordability:

◎: uniform solid printing, ejection failure was not observed even at the fine-line portion in all printed samples

○: slightly non-uniform solid printing, ejection failure was not observed even at the fine-line portion

△: non-uniform solid printing, ejection failure was not observed at the fine-line portion but printing position deviation was observed

×: irregular printing due to ejection failure was observed at the solid printing portion, and printing omission due to ejection failure was observed at the fine-line portion

××: ejection failure often occurs

[0098]

As shown in Table 2, the ink composition of the present invention shows good ink-jet recordability as well as good storage stability. In the same manner, the resulting ink composition before subjecting to the heating test was injected in a black pen of a piezoelectric jet type printer EM-900C manufactured by Epson Corp., and then the printing test was carried out.

Specifically, solid printing and fine-line printing were carried out using A4-size paper and the ejection state of the ink was observed. In the case of both ink compositions of the Examples and Comparative Examples, no problems were observed.

[0099]

[Effect of the Invention]

As explained above, the present invention provides a pigment dispersion for red or magenta ink-jet ink having high-level dispersion stability and a composition for ink-jet ink as well as particulate dispersion of pigment is achieved, by using a colored kneaded mixture for ink-jet comprising a quinacridone-based pigment, a quinacridone-based compound having substituent groups comprising phthalimido skeleton, a specific styrene-based resin and an alkali metal hydroxide. In particular, in case of applying to an ink for thermal ink-

jet recording, an ink composition having an excellent reliability in comparison to an ink composition produced by the conventional methods.

[Abstract]

[Problems to be solved by the Invention]

The present invention provides a water-based pigment dispersion for red or magenta ink-jet ink in which the dispersion has good initial dispersibility of coloring material (pigment), the dispersion state maintains over a long period and the dispersion has excellent long-term storage stability, and an ink composition thereof.

[Means for solving the problems]

The present invention provides a pigment dispersion for red or magenta ink-jet ink having high-level dispersion stability and a composition for ink-jet ink as well as particulate dispersion of pigment is achieved, by using a colored kneaded mixture for ink-jet comprising at least a quinacridone-based pigment, a quinacridone-based compound having substituent groups comprising phthalimido skeleton, a specific styrene-based resin, an alkali metal hydroxide and humectant. In particular, in case of applying to an ink for thermal ink-jet recording, an ink composition having an excellent reliability in comparison to an ink composition produced by the conventional methods.